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DEVELOPMENT OF IMPROVED CONVERSION COATING
FOR USE WITH CORROSION-INHIBITING WHITE PRIMER.

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INTRODUCTION

Object

To develop an improved conversion coating for use with the white paint primer developed in Phase I of this contract. The coating, when applied to 2219-T87 aluminum alloy sheet specimens, 6" x 4" x 1/16", should satisfactorily withstand testing in a salt spray atmosphere for 400-600 hours. This conversion coating should have the same general characteristics as specified in MIL-C-5541 A and should be compatible with liquid oxygen, when tested according to MSFC-Spec.-126A.

Recapitulation of Approaches

In the original literature search it became apparent that most of the attempts to up-grade chromate conversion coatings had concentrated on the coating solution itself. Many references describe variations in coating formulations which lead to improvements in corrosion resistance.¹⁻⁹ However, despite the large amount of effort expended, there is still no solution which will adequately protect 2219 alloy.

Accordingly, it was decided to study other aspects of the coating process, which have received less attention, as follows:

1. Study of surface pre-treatments. It is well-known in the art of metal finishing that the conditioning of the surface prior to coating can have a large effect on the properties of the coating. Since copper is the alloying element responsible for the poor corrosion resistance of 2219 alloy, the surface was treated with reagents which could be expected to remove copper preferentially from the surface, thus reducing the surface copper content. Alloys, such as 2024, with copper contents of 4.5%, compared to 6% for 2219, can be adequately protected with existing chromate treatments.¹⁰

Using specific reagents to remove harmful surface micro-constituents is a not uncommon practice, e.g. the use of hydrofluoric acid to remove silica prior to anodizing high-silicon alloys.

2. Application of a thin metallic coating to the alloy surface by an electroless process, either instead of, or prior to, a suitable conversion coating.

Introduction

3. Testing of modified conversion coating solutions which have proved effective for other copper - containing alloys, such as 2024. The essential constituents of "amorphous chromate" coating solutions - the most effective for protecting the high strength alloys - are: a hexavalent chromium compound, a fluoride, and an accelerator such as ferro - or ferri - cyanide, in an acid (usually nitric) solution. In addition, many additives such as zinc and cadmium salts⁷, hexavalent molybdenum and tungsten⁸, chloride ion¹² and others have been reported to improve the performance of these coatings. The way in which this is achieved is not generally understood. Several modifications of a standard chromate coating were applied to 2219 alloy.
4. Investigation of the possibility of post-treating the applied chemical film in order to seal or insolubilize it and thus render it more effective for protecting the alloy. Such sealing is common practice with anodized films, and methods have been described for other types of conversion coating.^{13,14}

Of the four approaches outlined, no. 1 seemed most likely, after some preliminary work, to lead to significant improvements in corrosion resistance. A metallic coating, as described under approach no. 2 would be heavy and does not have the general characteristics of a coating conforming to Military Specification MIL-C-3511 A. Accordingly, little work was done under this approach.

DISCUSSION OF RESULTS

Approach Number 1

A large number of reagents which could be expected to deplete the alloy surface of copper were investigated. Among these were solutions of: nitric acid; ammonium persulfate¹⁵; mercuric chloride; ammonia; bromine; ferric chloride; cuprous chloride¹⁵; chromic acid¹⁵; hydrogen peroxide¹⁶; sodium sulfide/sulfur, followed by treatment with potassium cyanide¹⁶. Also examined was ammonium fluoride which is reported to passivate an aluminium surface¹⁷.

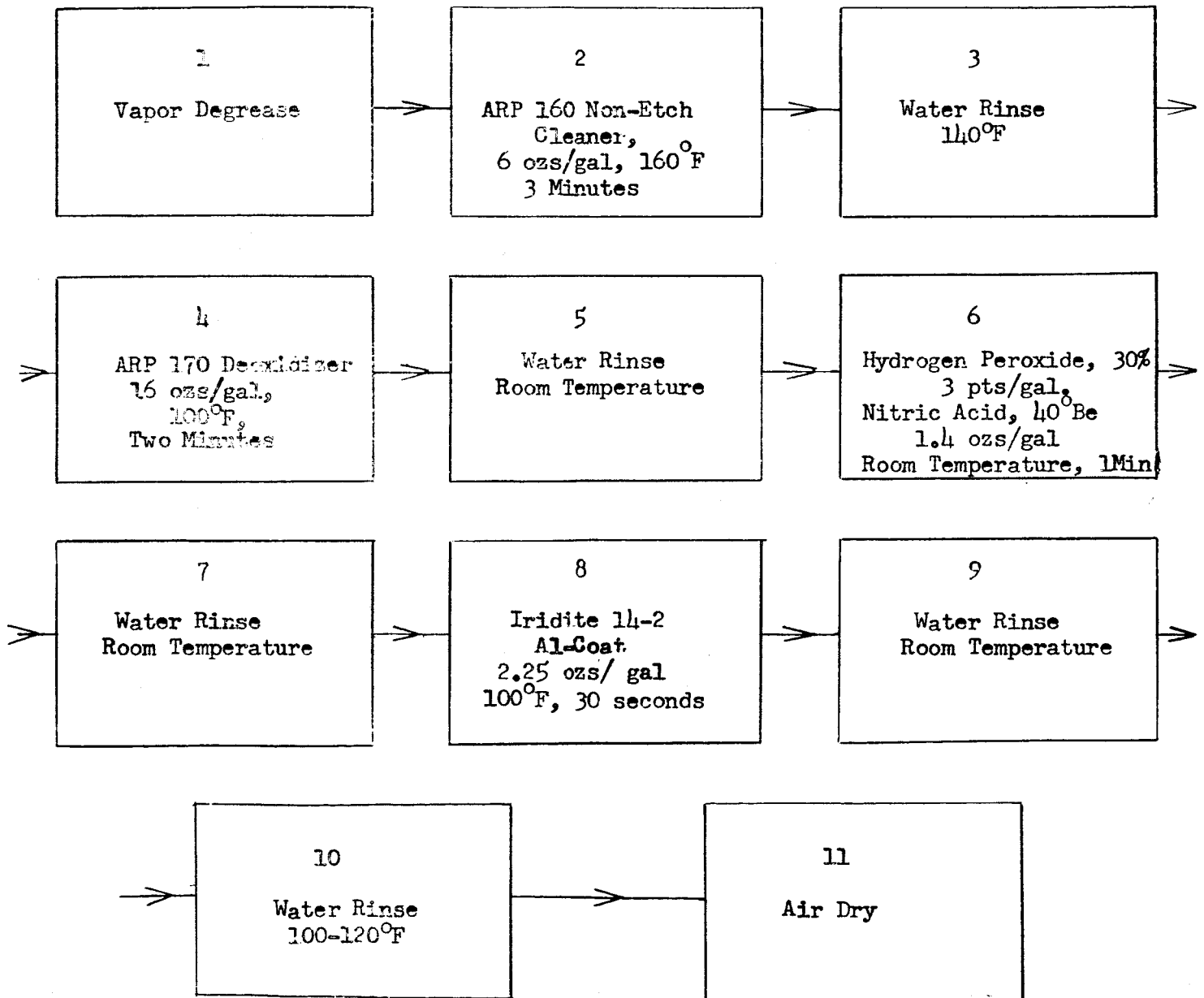
Several of these reagents could not be used because they had an etching or pitting action on the alloy surface. Those reagents which would rapidly dissolve copper aluminide (the intermetallic in which most of the copper is present in the alloy), without having a deleterious effect on the surface of 2219 alloy itself, were used to pre-treat 2219 alloy panels, which were then conversion - coated by the Iridite 14-2 process. Panels were exposed to salt - spray and the number of hours to pitting recorded.

This preliminary, qualitative work indicated that panels treated with acidic solutions of hydrogen peroxide or ammonium persulfate gave a substantial improvement in corrosion resistance, compared to panels not so pre-treated. A nitric acid solution of ammonium fluoride gave a small improvement.

An optimum pre-treatment and coating system was selected by comparing hydrogen peroxide and ammonium persulfate, at two concentration levels, and other system variables, using a thirty-two panel, fractional - factorial experimental design.

Discussion of Results

The number of hours before thru pits appeared on the panels ranged from 23 to 212. Analysis of the results predicts a salt spray test life of 237 hours for this optimized coating schedule:



Discussion of Results

This process consists of the Iridite 14-2 process, with insertion of the acidic hydrogen peroxide pre-treatment. No explanation is offered of the way in which this solution modifies the surface so as to render the chromate conversion coating more effective.

Approach Number 2

As mentioned above, little work was done using this approach.

Approach Number 3

Many modifications of chromate conversion coatings have been claimed to give enhanced corrosion resistance. However, there are few references to the protection of 2219 alloy with such solutions. Therefore, several such solutions were applied to 2219 alloy and salt-spray tested using Iridite 14-2 as control.

It is known that different metal cations have marked effects on the corrosion resistance of conversion coatings.^{3,5,7,18} Conversion coatings were prepared, containing small amounts of nickelous, cobaltous and cupric salts, and applied to 2219 alloy. On exposure to salt spray, these panels corroded slightly more slowly than panels protected with Iridite 14-2.

In another panel series, the effect of replacing varying amounts of hexavalent chromium with hexavalent molybdenum was tried. Under salt spray, the performance of these modified coatings was inferior to that of Iridite 14-2.

No other modified conversion coatings gave significant improvements over Iridite 14-2 and even in the case of coatings containing Ni^{2+} , Co^{2+} , and Cu^{2+} ions, the improvements were less marked than those obtained from the use of the pre-treatments described under Approach 1.

An interesting observation was that coating solutions containing substantial amounts of chloride ion⁴ had a deleterious effect on the alloy, causing pitting while in the processing bath. Similar effects were observed in the case of other chloride - containing solutions. It appears that chloride ion is particularly harmful to this class of alloy and this is further evidenced by the poor resistance to corrosion in salt - laden atmospheres.

Discussion of Results

Approach Number 1

A freshly applied chromate conversion coating film is a gel of complex composition. It contains soluble species, such as hexavalent chromium, which are leached out under salt spray, thus diminishing the protective value. If the coating were post-treated with a heavy metal solution, so as to produce an outer layer of insoluble, heavy metal chromate, the rate at which chromate is leached from the coating might be expected to be reduced.

2219 alloy panels, freshly coated with Iridite 14-2 conversion coating, were treated with ceric ammonium nitrate solution. Under salt spray, these panels corroded more slowly than panels not so post-treated, but the difference was very small.

EVALUATION OF RESULTS

Since the standard deviations obtained from salt spray test data are large, only large differences between the times-to-corrode of test and control panels can be taken as significant in a single comparison test. For this reason only Approach 1 was considered to have given, in preliminary semi-quantitative testing, results worth pursuing.

The data obtained, when the results of preliminary work under Approach 1 were checked by means of a statistically designed experiment, reinforced the conclusion that a suitable chemical pre-treatment of the alloy improves the performance of a subsequently applied conversion coating.

The predicted salt spray life of 237 hours for the optimum coating schedule is greater than the 168 hours⁺ life required by MIL-C-5541 A, suggesting that the process could be made the means of satisfactorily protecting 2219 alloy, according to the requirements of MIL-C-5541 A.

EXPERIMENTAL

Preparation of Treatment Solutions

Technical grade chemicals were used where available. In a few cases reagent grade was used. Solutions were made up in tap water, except in the final, statistical experiment, where distilled water was used.

Iridite 14-2 Al-Coat supplied by Allied Research Products Inc., and used throughout as control. Solutions were prepared in the manner recommended by the supplier.

Panel Preparation and Testing

2219-T87 alloy panels, 6" x 4" x 1/16" were furnished by N.A.S.A. They were treated in baths of glass, polyethylene or stainless steel, of 1-2 liters capacity.

Coated panels were exposed in a salt spray cabinet, under the conditions specified in Method 822.1 of Federal Test Method Standard No. 151a. In the preliminary work, panels were exposed for a period, usually 168 hours and the extent of corrosion compared with that on the control panels. This gave a direct semi-quantitative measure of relative rates of corrosion for test and control coatings.

In the later work, the method as required by N.A.S.A. was followed. Panels were examined daily and washed with distilled water prior to inspection. They were retired when three definite pits had appeared on the significant surface. This criterion of failure proved to be difficult to use, since it is often difficult to distinguish developing pits from the black streaks which always appear after a few hours under salt spray. Also the significant surface may erupt in a rash of minute pits, making it difficult to estimate when the coating should be said to have failed. These factors contribute to the large standard deviation, mentioned above, of 34 hours.

LOX - Compatibility Testing

2219-T87 specimens, 1/16" x 11/16" dia., were furnished by N.A.S.A., coated by the procedure described above for panels, and submitted to N.A.S.A. for testing.